

Template Synthesis, Crystal Structure, and Magnetic Properties of a Dinuclear Copper(II) Complex with Cooperative Hydrogen Bonding

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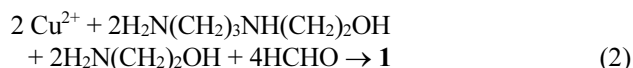
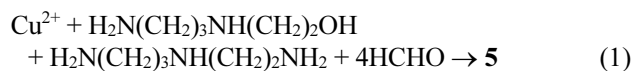
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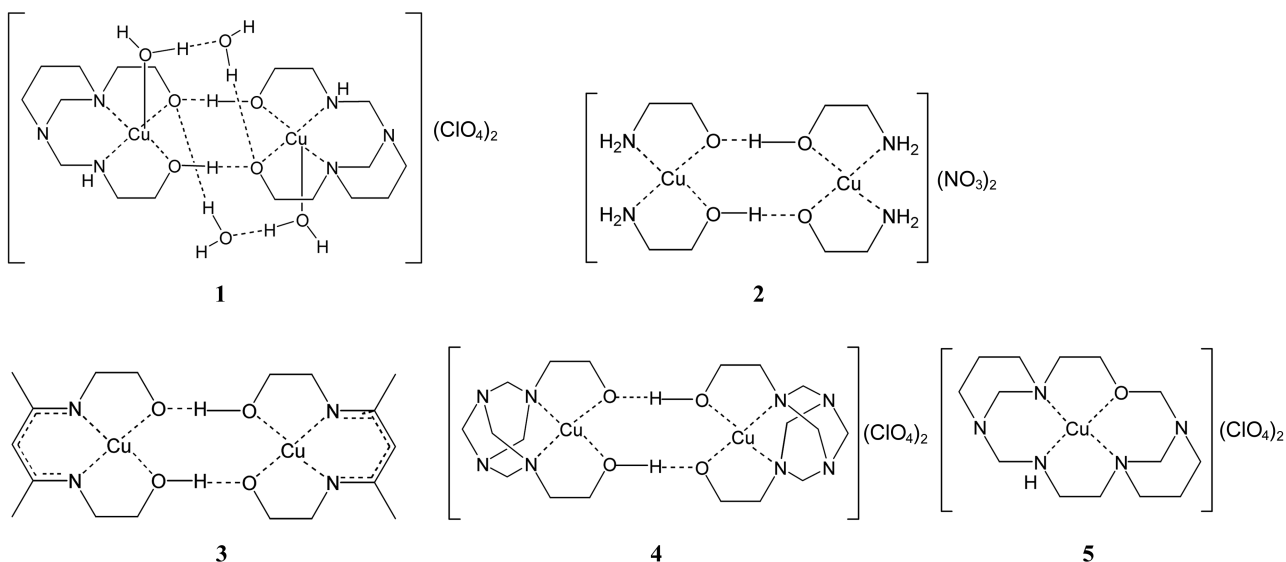
Key Words : Metal-directed condensation, Cooperative hydrogen bond, Dinuclear copper(II) complex, X-ray structure, Magnetic interactions

The design and synthesis of polynuclear transition metal complexes have received much attention because of their potential applications in various fields, such as catalysis, supramolecular chemistry, and materials chemistry.¹⁻⁹ Until now, various types of dinuclear copper(II) complexes have been prepared and investigated. Some dinuclear copper(II) complexes resulting from cooperative hydrogen bonding, such as **2-4** containing two N₂O₂ donor sets, are also reported.⁶⁻⁹ In **2-4**, each mononuclear unit contains both hydrogen-bond donor and acceptor groups. It has been revealed that the Cu-O distances of **2** and **4** are shorter than the Cu-N (primary or tertiary amino groups) distances.⁷ In the case of **3**, however, the Cu-O distances are longer than the Cu-N (imino groups) distances. The O-H···O and the Cu···Cu distances of **2-4** are influenced by their structural characteristics.⁶⁻⁸ Furthermore, **2-4** are known to exhibit antiferromagnetic coupling. However, examples of such dinuclear copper(II) complexes with cooperative hydrogen bonding are relatively few, and the effects of the structural features on the hydrogen bonding and the antiferromagnetic coupling remain poorly understood. Therefore, we have been interested in the preparation of various types of dinuclear copper(II) complexes containing two N₂O₂ donor

sets that linked together by cooperative hydrogen bonding.



A variety of copper(II) complexes have been prepared by metal-directed condensation involving amines and formaldehyde. For example, the mononuclear complex **5** has been prepared by the reaction of Eq. (1).¹⁰ In this work, we prepared new hydrogen-bonded dinuclear copper(II) complex [Cu(L¹)(H₂O)]₂(ClO₄)₂·2H₂O (**1**) (HL¹=1-(2-hydroxyethylaminomethyl)-3-hydroxyethyl-1,3-diazacyclohexane) from the reaction of Eq. (2). In contrast to **2-4**, **1** consists of two unsymmetrical mononuclear units; one 2-hydroxyethyl group of HL¹ is attached to the secondary amino group, and the other to the tertiary amino group. Therefore, the present system offers a further opportunity to understand the deprotonation behaviors of the *N*-hydroxyethyl groups. Synthesis, crystal structure, and chemical properties of **1** are reported. The structural features and magnetic properties of **1** are compared with those of **2-4**.



Experimental

Measurements. Infrared spectra were recorded with a Genesis II FT-IR spectrometer, electronic absorption spectra with an Analytik Jena Specord 200 UV/vis spectrophotometer, and conductance measurements with a Metrohm Herisau Conductometer E518. FAB-mass spectra were performed at the Korea Basic Science Institute, Daegu, Korea. Elemental analyses were performed at the Research Center for Instrumental Analysis, Daegu University, Gyeongsan, Korea. Magnetic susceptibility measurements were performed at the Korea Basic Science Institute, Seoul, Korea; the experiments were carried out in an applied field of 1000 Oe between 2 and 300 K on a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer. Diamagnetic corrections were made by using Pascal's constants.

Preparation of $[\text{Cu}(\text{L}^1)(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (1**) ($\text{HL}^1 = 1$ - $(2$ -hydroxyethylaminomethyl)- 3 -hydroxyethyl- $1,3$ -diazacyclohexane).** A methanol solution (*ca.* 30 mL) of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (3.0 g, 15 mmol), 2-(3-aminopropylamino)ethanol (1.8 mL, 15 mmol), 2-aminoethanol (0.9 mL, 15 mmol), and 35% formaldehyde (5.2 mL) was stirred for > 24 h at room temperature. After the addition of NaClO_4 (*ca.* 2.0 g), the mixture was stored in a refrigerator to precipitate a blue solid. The product was collected by filtration, washed with methanol, and dried in air. The pure product was obtained by fractional recrystallizations of the crude product from hot water-acetonitrile (1:1). Yield: ~50%. *Anal.* Found: C, 27.07; H, 6.17; N, 10.70. Calc. for $\text{C}_{18}\text{H}_{48}\text{N}_6\text{CuCl}_2\text{O}_{16}$: C, 26.94; H, 6.03; N, 10.47%. FAB mass (m/z): 631.7 ($[\text{Cu}_2(\text{L}^1)_2 + \text{ClO}_4]^\pm$), 530.6 ($[\text{Cu}_2(\text{L}^1)_2 - \text{H}^\pm]^\pm$). IR (Nujol mull, cm^{-1}): 3200 ($\nu\text{N-H}$), 3360 ($\nu\text{O-H}$), 3520 ($\nu\text{O-H}$, H_2O), 1100, ($\nu\text{Cl-O}$, ClO_4).

Crystal Structure Determination. Single crystals of **1** suitable for X-ray diffraction analysis were obtained by slow evaporation of water-acetonitrile (1:1) solution of the complex. Structural measurement for the compound was performed on a STOE STADI4 four-circle diffractometer using graphite monochromatized Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) at 298(2) K. The unit cell parameters were calculated by least-squares fit of 2θ reflections in the ranges of $9.5 < \theta < 10.5^\circ$. Intensities of three reflections monitored periodically exhibited no significant variation. The structure was solved by direct method and refined on F^2 by full-matrix least-squares procedures.¹¹ All non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms were included in the structure factor calculation at idealized positions by using riding model, but not refined.

Results and Discussion

Crystal Structure. The dinuclear copper(II) complex **1** was prepared by the reaction (Eq. (2)) of formaldehyde with 2-(3-aminopropylamino)ethanol and 2-aminoethanol in the presence of Cu^{2+} ion. The ORTEP drawing of the mononuclear unit $[\text{Cu}(\text{L}^1)(\text{H}_2\text{O})](\text{ClO}_4) \cdot \text{H}_2\text{O}$ in **1** with the atomic

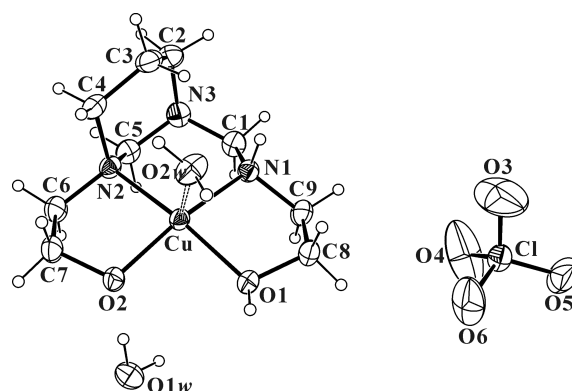


Figure 1. An ORTEP drawing of $[\text{Cu}(\text{L}^1)(\text{H}_2\text{O})](\text{ClO}_4) \cdot \text{H}_2\text{O}$ in **1**.

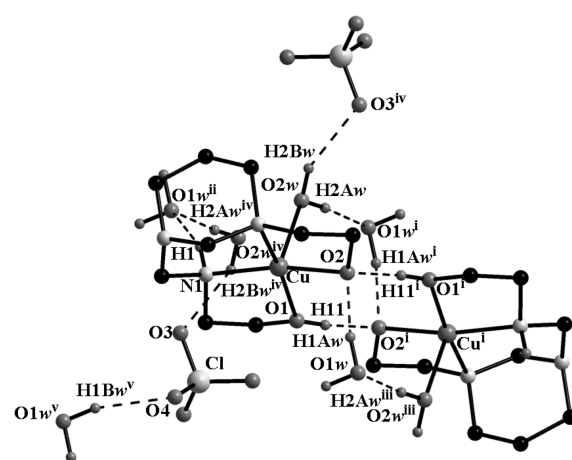


Figure 2. A view of the dimer **1** showing hydrogen bonds. The hydrogen bonds are shown as dotted lines. Symmetry code: (i) 1-x, 1-y, 1-z; (ii) 1+x, y, z; (iii) 1-x, 1-y, 1-z; (iv) 2-x, 1-y, 1-z; (v) 1-x, 1-y, -z.

numbering scheme is shown in Figure 1. Figure 2 shows that **1** consists of two mononuclear units that are linked together by two hydrogen bonds and has an inversion center between the two metal ions. Two oxygen atoms {O(1) and O(2)} as well as the secondary and tertiary nitrogen atoms {N(1) and N(2)} are coordinated to the metal ion. The coordination geometry of each mononuclear unit is distorted square-pyramid with a water molecule at the apical position. The O(2) atom *trans* to the N(1) atom is involved in the *N*-ethoxo group, whereas the O(1) atom is involved in the *N*-hydroxyethyl group. This clearly shows that the coordinated *N*-hydroxyethyl group *trans* to the secondary amino group is more readily deprotonated than that *trans* to the tertiary amino group. The six-membered chelate ring as well as the 1,3-diazacyclohexane ring has stable chair conformation. The apical water molecule {O(2w)} and *N*- $\text{CH}_2\text{CH}_2\text{CH}_2$ -*N* are *syn* with respect to the six-membered chelate ring.

The Cu atom is displaced by *ca.* 0.025 Å from the mean N_2O_2 plane toward the apical water molecule. Table 2 shows that the Cu-N(1) (secondary amine) distance (2.015(3) Å) is shorter than the Cu-N(2) (tertiary amine) distance (2.042(3) Å), as usual. The Cu-O(2) distance (1.926(2) Å) involved in the *N*-ethoxo group is distinctly shorter than the Cu-O(1)

Table 1. Crystal Data and Structure Refinement for **1**

Empirical formula (<i>M</i>)	C ₉ H ₂₄ ClCuN ₃ O ₈ (401.30)
Crystal system (space group)	monoclinic (<i>P</i> 2 ₁ / <i>n</i>)
<i>a</i> / <i>b</i> / <i>c</i> (Å)	7.8730(8)/23.634(2)/9.3619(9)
β (°)	108.379(7)
<i>V</i> (Å ³)	1653.1(3)
<i>Z</i>	4
<i>D</i> _{calc} (g cm ⁻³)	1.612
μ (cm ⁻¹)	1.523
<i>F</i> (000)	836
θ range for data collection (°)	1.72–27.45
Absorption correction	T _{min} = 0.6527, T _{max} = 0.9029
Index ranges	−10 ≤ <i>h</i> ≤ 9, 0 ≤ <i>k</i> ≤ 30, 0 ≤ <i>l</i> ≤ 12
Reflections collected	3777
Independent reflections	3777
Reflections observed (> 2σ)	3273
Data Completeness	99.8
Data / restraints / parameters	3777 / 0 / 200
Goodness-of-fit on <i>F</i> ²	1.060
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.045, <i>wR</i> ₂ = 0.121
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.054, <i>wR</i> ₂ = 0.131
Largest diff. peak and hole (eÅ ⁻³)	0.86 and −0.55

Table 2. Bond Distances (Å) and Angles (°) of **1**

Cu-O(1)	1.994(2)	Cu-O(2)	1.926(2)
Cu-N(1)	2.015(3)	Cu-N(2)	2.042(3)
Cu-O(2 <i>w</i>)	2.325(2)	O(1)-C(8)	1.434(4)
N(1)-C(1)	1.509(4)	N(1)-C(9)	1.494(4)
N(2)-C(4)	1.492(4)	N(2)-C(5)	1.505(4)
N(3)-C(1)	1.437(5)	N(3)-C(2)	1.470(5)
N(3)-C(2)	1.433(5)	Cu⋯Cu ⁱ	5.037(2)
O(1)⋯O(2) ⁱ	2.531(3)	O(1)-H(11)	0.820
O(1)-Cu-O(2)	91.2(2)	O(1)-Cu-N(2)	168.6(2)
O(2)-Cu-N(1)	169.6(2)	O(1)-Cu-N(1)	84.2(2)
O(2)-Cu-N(2)	86.9(2)	N(1)-Cu-N(2)	95.7(2)
O(1)-Cu-O(2 <i>w</i>)	90.7(2)	O(2)-Cu-O(2 <i>w</i>)	95.2(2)
N(1)-Cu-O(2 <i>w</i>)	94.2(2)	N(2)-Cu-O(2 <i>w</i>)	100.7(2)
C(1)-N(3)-C(2)	117.5(3)	C(1)-N(3)-C(5)	114.7(3)
C(2)-N(3)-C(5)	112.1(3)		

Symmetry code: (i) 1 -*x*+1, -*y*, -*z*+1

distance (1.994(2) Å). The in-plane Cu-O(1) and Cu-O(2) distances are shorter than the Cu-N distances. The apical Cu-O(2*w*) (H₂O) distance (2.325(2) Å) is considerably longer than the in-plane Cu-O and Cu-N distances. The N(1)-Cu-N(2) angle (95.7(2)°) involved in the six-membered chelate ring is larger than the O(1)-Cu-O(2) angle (91.2(2)°). The O(1)-Cu-N(2) and O(2)-Cu-N(1) angles (168.6(2) and 169.6(2)°, respectively) are deviated from 180°. The O-Cu-O(2*w*) and N-Cu-O(2*w*) angles are also deviated from 90°. The N(3)-C distances (1.433(5)-1.470(5) Å) are distinctly shorter than other N-C bond distances. Furthermore, C-N(3)-C angles (112.1(3), 114.7(3), and 117.5(3)°) are larger than 109.4°. This indicates the sp³-hybridized N(3) atom is restrained because of the angle strain arising from the ring

Table 3. Specified Hydrogen Bond Geometry (Å, °) for **1**

Donor(D)-H⋯ Acceptor(A)	<i>d</i> (D-H)	<i>d</i> (H⋯A)	<i>d</i> (D⋯A)	Angle (D-H⋯A)
O(1)-H11⋯O(2) ⁱ	0.82	1.72	2.531(3)	168.8
O1 <i>w</i> -H1A <i>w</i> ⋯O(2)	0.96	1.76	2.704(4)	168.2
O2 <i>w</i> -H(2A)⋯O1 <i>w</i> ⁱ	0.87	1.92	2.786(4)	171.4
O1 <i>w</i> -H1B <i>w</i> ⋯O4 ⁱⁱⁱ	0.90	2.08	2.952(6)	164.7
O2 <i>w</i> -H2B <i>w</i> ⋯O3 ^{iv}	0.89	2.15	2.978(6)	154.5
N1-H1⋯O1 <i>w</i> ⁱⁱ	0.91	2.16	3.006(4)	153.7

Symmetry codes: (i) -*X*+1, -*Y*+1, -*Z*+1; (ii) *X*+1, *Y*, *Z*; (iii) -*X*+1, -*Y*+1, -*Z*; (iv) -*X*+2, -*Y*+1, -*Z*+1.**Table 4.** Structural Features (Å) and Magnetic Parameters of the Complexes

Complex	Cu⋯Cu	O⋯O ^a	Cu-N ^a	Cu-O ^a	<i>g</i>	2 <i>J</i> , cm ⁻¹
1	5.038(2)	2.527(4)	2.032	1.962	2.07	-18.8
2^b	4.941	2.452	1.990	1.958	2.11	-56
3^c	4.979(6)	2.29(1)	1.90	1.947	2.04	-94
4^d	4.555	2.459	2.003	1.947	2.11	-4.1

^aAverage value of Cu-N or Cu-O distances. ^bRef. 6. ^cRef. 7. ^dRef. 8.

rigidity of the ligand. The O(1)⋯O(2)ⁱ distance (2.531(3) Å) shows that two mononuclear units of **1** are linked together by relatively strong hydrogen bonds. One of the most remarkable structural features of the complex is that each lattice water molecule acts as a bridge between the two mononuclear units through hydrogen bonds; the O(2) atom of one mononuclear unit and the O(2*w*)ⁱⁱⁱ atom of the coordinated water molecule are hydrogen bonded to the water molecule involving O(1*w*) atom (Figure 2 and Table 3). This also contributes to the stability of **1** as the dimeric form.

Table 4 shows that the average Cu-N and Cu-O distances (2.032 and 1.962 Å, respectively) of **1** are longer than those of **2-4**.⁶⁻⁸ The O(1)⋯O(2)ⁱ distance (2.531(3) Å) of **1** is also longer than the distances (2.29-2.46 Å) of **2-4**. As a result, the Cu⋯Cu distance (5.037(2) Å) is longer than those (4.555-4.979 Å) of **2-4**.

Spectra and Properties. The dinuclear complex **1** is quite stable in the solid state and in various solvents, such as nitromethane, acetonitrile and water. The molar conductance values of **1** measured in nitromethane (162 Ω⁻¹mol⁻¹cm²), acetonitrile (270 Ω⁻¹mol⁻¹cm²), and water-acetonitrile (3:1) (198 Ω⁻¹mol⁻¹cm²) indicate that the complex is a 1:2 electrolyte. FAB mass spectrum of **1** measured in acetonitrile shows two groups of peaks corresponding to [Cu₂(L¹)₂+ClO₄]⁺ and [(Cu₂(L¹)₂-H⁺)]⁺ fragments at *m/z* 631.7 and 530.6, respectively. The electronic absorption spectrum of **1** measured in Nujol mull shows a d-d band at 590 nm, which is comparable with those of other square-pyramidal copper(II) complexes with N₂O₃-donor sets.^{5,9,12} The spectra measured in nitromethane, acetonitrile, and acetonitrile-water (1:3) also show the band at 594 (ε = 103 M⁻¹cm⁻¹), 588 nm (ε = 110 M⁻¹cm⁻¹), and 600 nm (ε = 115 M⁻¹cm⁻¹), respectively. Electronic and FAB mass spectra of **1** as well as the molar conductance values strongly indicate that the

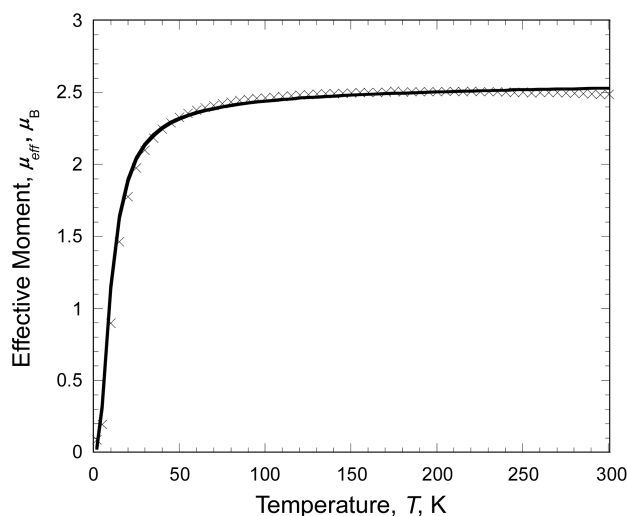


Figure 3. Fitting of effective magnetic moment versus temperature (K) data of **1** using dimer model of $S = 1/2$ local spin. Solid line shows the best fit obtained.

hydrogen bonds between the two mononuclear units are so strong that the complex is quite stable as the dinuclear form even in the polar solvents. Although **1** is quite stable in the solvents, it is rapidly decomposed in acidic aqueous solutions; the decomposition reaction rate in 0.1 M HClO₄ aqueous solution was found to be too fast to be measured by the ordinary method.

Magnetic susceptibilities (χ) of **1** were measured from 2 to 300 K to see the effects of the structural parameters on the magnetic properties. The effective magnetic moment, ($\mu_{\text{eff}} = (8\chi_M T)^{1/2}$), is 2.49 μ_B/Cu_2 at room temperature. The value is slightly larger than 2.45 μ_B expected for independent two copper(II) ions ($S = 1/2$, Cu(II), $g = 2$). Figure 3 shows that $\mu_{\text{eff}}(T)$ decreases monotonically as the temperature is lowered, indicating a weak antiferromagnetic interaction between the Cu(II) ions. The $\mu_{\text{eff}}(T)$ data was fit to an analytical expression for $c(T)$ for a coupled $S = 1/2$ dinuclear spin model (Eq. (3)) based on the Hamiltonian $H = -2JS_1 \cdot S_2$ ($S_1 = S_2 = 1/2$).¹³ The fitting leads to a value of $2J = -18.8 \text{ cm}^{-1}$ with $g = 2.07$ and a value of temperature independent paramagnetism (TIP) = $60 \times 10^{-6} \text{ emu/mol}$. The relatively long Cu...Cu distance (5.038(2) Å) within the hydrogen-bonded dimer rules out direct interaction between the metal ions. Therefore, the antiferromagnetic coupling between two copper(II) ions of **1** may be attributed to a superexchange through the cooperative hydrogen bonds.

$$\chi_M = \frac{2N\beta^2 g^2}{3kT} \left[1 + \frac{1}{3} \exp(-2J/kT) \right]^{-1} + \text{TIP} \quad (3)$$

The structural features of **1-4** and their magnetic parameters are listed in Table 4 for comparison. It is seen that the antiferromagnetic coupling for **1** is stronger than that for **4**, in spite of its relatively long Cu...Cu and O...O distances. Unfortunately, we could not find any direct correlation between the coupling constants and the structural features of the complexes.

Summary

The dinuclear complex **1** with cooperative hydrogen bonds can be prepared by the metal-directed reaction of Eq. (2). This work shows that the coordinated hydroxyl group *trans* to the secondary amino group is deprotonated more readily than that *trans* to the tertiary amino group and acts as the hydrogen-bond acceptor. The lattice water molecules in **1** act as bridges between the two mononuclear units through hydrogen bonds. The complex is quite stable as the dimeric form even in various polar solvents. The complex exhibits a weak antiferromagnetic interaction between the metal ions in spite of relatively long Cu...Cu distance. This strongly supports the suggestion that the antiferromagnetic behavior is closely related to the cooperative hydrogen bonds.

Supplementary Material. Crystallographic data for **1** have been deposited with the Cambridge Crystallographic Data Center (CCDC number 800643). Copies of the data may be obtained free of charge, on application to the director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (<http://www.ccdc.cam.ac.uk>, fax: +44-1233-336-033, or e-mail: deposit@ccdc.cam.ac.uk).

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